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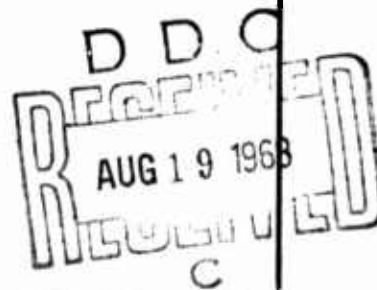


THESIS

RESISTANCE AND CAPACITANCE MEASUREMENTS
ON LAMELLAR GRAPHITE-AMMONIA COMPOUNDS

by

Kinnison Henry Thomas



June 1968

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RESISTANCE AND CAPACITANCE MEASUREMENTS
ON LAMELLAR GRAPHITE-AMMONIA COMPOUNDS

by

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Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

from the

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ABSTRACT

The theory of spontaneous polarization in ferroelectric solids leading to an infinite value in the dielectric constant is developed from classical electrodynamics and thermodynamics. The nature of the lamellar graphite compounds is discussed and similarities in the structure of one of these, the graphite-ammonia compound, to a recognized ferroelectric, Potassium Ferrocyanide Trihydrate, is pointed out. The details of the equipment and the procedure necessary to form the lamellar graphite-ammonia compound using pyrolytic graphite and to test the compound to determine if it exhibits ferroelectric properties are discussed. Ferroelectricity in the graphite-ammonia compound was not observed. Differences in the results obtained using pyrolytic graphite and those obtained using polycrystalline graphite by other observers to form the graphite-ammonia compound are pointed out and discussed.

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1. Introduction

The fact that certain materials, ferroelectrics, would exhibit electric behavior in many respects analogous to the magnetic behavior of ferromagnetic materials is now well established. It was first recognized by Haiblutzel in 1939 in Rochelle salt, the sodium-potassium salt of tartaric acid, and has since been found to be present in many dielectrics (1). One ferroelectric compound that has been studied extensively is potassium ferrocyanide trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$ (KFCT). KFCT crystalizes in a repetitive layered structure, every third layer being a layer of the hydrated water molecules (7). The ability of graphite to form compounds by the inclusion of foreign substances within its structure has been known for more than a century (1). In what follows the author will show that the structure of the graphite-ammonia compound is in some respects analogous to KFCT and that one might expect it to also exhibit ferroelectric properties.

In this section we will do three things: present a phenomenological theory of one of the most striking features of a ferroelectric; describe the nature of the lamellar graphite compounds; show that one of these, namely the graphite-ammonia compound, could exhibit ferroelectric properties. The purpose of this work has been to discover if this compound is ferroelectric.

Let us begin by investigating the relationship between the dielectric constant, which is a readily measurable quantity in the laboratory, and the polarizability of an atom or molecule at a

lattice site. The polarizability, α , is defined as the ratio between the induced dipole moment of the atom or molecule, p , and the local electric field at the lattice site E_{loc} :

$$\alpha = p/E_{loc},$$

$$p = \alpha E_{loc},$$

or

and the total polarization is given by

$$P = N\alpha E_{loc}$$

where N is the number of atoms or molecules per unit volume.

E_{loc} is the macroscopic field in the dielectric, E , modified by the presence of neighboring dipoles. For simplicity let

$$P = N\alpha (E + 4\pi P/3) \quad (1-1)$$

which assumes that $E_{loc} = E + 4\pi P/3$ where $4\pi P/3$ is a contribution from the field produced by the polarization of other atoms or molecules in the vicinity of the site. This contribution was calculated first by Lorentz and is the electric field at the center of a fictitious spherical cavity resulting from polarization charges on the surface of the sphere, plus a depolarization field from polarization charges on the outer surface of the specimen. It assumes simple cubic symmetry in the dielectric. Solving equation (1-1) for the electric susceptibility one obtains:

$$\frac{P}{E} = \frac{N\alpha}{1 - (4\pi/3) N\alpha} \quad (1-2)$$

The dielectric constant is defined as

$$\epsilon = 1 + 4\pi (P/E),$$

so

$$\frac{\epsilon-1}{4\pi} = \frac{\sum N\alpha}{1 - (4\pi/3) \sum N\alpha} \quad (1-3)$$

This is the Clausius-Mossotti relation, which is commonly used to evaluate the atomic polarizability from measurements of the dielectric constant. It should be noted that this relation indicates that the dielectric constant for any material will become infinite whenever $\sum N\alpha$ equals $3/4\pi$, which we know is not the case.

In deriving the Clausius-Mossotti relation we have neglected the fact that many molecules have permanent dipole moments due to some kind of asymmetry in their structure. When these polar molecules condense into the solid state as weakly bound molecular crystals, they retain their structural identity, and more important for the present consideration, they retain their dipole moments. If the dipoles were isolated, they would tend to line up in the presence of an electric field because the potential energy of a dipole in an electric field is a minimum when p and E are parallel. Actually the molecular dipoles are not isolated, and because of their thermal energy they are continually vibrating and rotating about an equilibrium position in the solid. Thus when an electric field is applied the dipoles are perturbed in trying to line up in the field. The higher the temperature, the greater the thermal energy, the greater the perturbation, and the less the average polarization. The effective dipole moment of a polar molecule in the direction of an electric field is $p \cos \theta$, where p is the dipole moment and θ is the average

angle between the dipole moment and the electric field. If there are N dipoles per unit volume, the polarization is given by

$$P = N p \cos \theta. \quad (1-4)$$

If we apply Boltzmann statistics to calculate the average angle we find that

$$\cos \theta = \coth a - 1/a,$$

or the Langevin function, $L(a)$, where $a = pE/kT$.

For high temperature solving equation (1-4) for the polarizability, we find

$$\alpha = p^2/3 kT, \quad (1-5)$$

in the limit where a approaches zero or pE is much less than kT .

Equation (1-4) is the Curie-Langevin formula for the polarizability.

Substituting the Langevin temperature dependence for α into the Clausius-Mossotti relation, equation (1-3), the denominator becomes

$$1 - T_c/T$$

where

$$T_c = \frac{4}{3} \frac{p^2 N}{3k} \quad (1-6)$$

and,

$$\begin{aligned} \epsilon &= 1 + \frac{4\pi \sum N p^2 / (3kT)}{1 - T_c/T} \\ &= 1 + \frac{g}{(T - T_c)}, \end{aligned} \quad (1-7)$$

g being a finite constant of the medium. Equation (1-7) is commonly known as the Curie-Weiss law where T_c is the transition or Curie temperature. If T equals T_c the denominator approaches zero, and

the dielectric constant will become infinite. We will show in what follows that at this temperature or below we could have polarization in the absence of an electric field, which is the phenomenon of ferroelectricity. Looking at equation (1-6) for water we can calculate the T_c to be approximately equal to 1200°K , which says that below 1200°K water would be ferroelectric, a statement that is obviously inconsistent with the facts. Our fallacious assumption was that the local field was given by the average field in the medium plus a contribution given by the Lorentz relation, which assumes that the lattice has cubic symmetry, and that all the dipoles are pointed in the same direction. This works well for induced dipoles, but as we have seen, it is not true for permanent dipoles. Essentially, it is the $4\pi/3$ factor for the local field that does not apply in equation (1-1). This does not mean that there is no local field in dipolar solids, only that the factor λ in the generalized formula $E_{\text{loc}} = E + \lambda P$ is much less than $4\pi/3$, probably even less than one.

We can approach the same problem from thermodynamic theory, which has the advantage of being independent of any particular atomic model. If we consider a solid that is ferroelectric for temperatures T less than T_0 , with no external pressure and no applied field, the Gibbs free energy at a given temperature will be a minimum if the material is in thermal equilibrium with its surroundings. Setting the free energy of the unpolarized crystal equal to zero, the free energy of the polarized crystal can be expanded as a power series of the polarization as

$$G(P,T) = \frac{1}{2}c_1P^2 + \frac{1}{4}c_2P^4 + \frac{1}{6}c_3P^6 + \dots$$

where the coefficients c are functions of temperature. Expanding in even powers of P only insures that the free energy is the same for "positive" and "negative" polarization along the polar axis, assuming for simplicity that in the ferroelectric region the spontaneous polarization occurs along a single axis. At thermal equilibrium in the absence of external electric fields (dG/dP) equals zero if G is to be a minimum, and the spontaneous polarization P_s satisfies the equation

$$0 = c_1P_s + c_2P_s^3 + c_3P_s^5 + \dots \quad (1-7)$$

If c_1 , c_2 , and c_3 are all positive, the root P_s equals zero will correspond to the only minimum of the free energy and spontaneous polarization would not occur. However, if as a result of the temperature dependence the coefficient c_1 would become negative there would be at least one non-vanishing value for P_s for which the free energy would be a minimum, or spontaneous polarization would occur. Consequently, if c_1 changes continuously with temperature from a positive to a negative value the equilibrium state of the medium changes from an unpolarized to a spontaneously polarized state at T equals T_0 . Let c_1 be defined as a constant, C , times the quantity $(T - T_0)$. If c_2 is positive, nothing new is added by the term in c_3 , which may then be neglected. Thus the polarization for zero applied electric field is given by

$$dG/dP = 0 = C(T - T_0)P_s + c_2 P_s^3 \quad (1-9)$$

so that either P_s equals zero or P_s^2 equals $(C/c_2) \cdot (T_0 - T)$.

For T greater than T_0 the only real root of equation (1-9) is at P_s equals zero, because C and c_2 are positive. Thus T_0 is the Curie temperature. For T less than T_0 the minimum free energy as a function of temperature is given by

$$P_s = (C/c_2)^{1/2} (T_0 - T)^{1/2}. \quad (1-10)$$

Equation (1-10) is plotted in Figure 1, and shows the onset of spontaneous polarization as a function of temperature.

If we now apply a small electric field to the medium, we may write according to thermodynamics

$$dG = -S dT + E dP.$$

Hence the applied electric field may be written

$$E = \left(\frac{\partial G}{\partial P} \right)_T$$

and we obtain E equals $c_1 \cdot P$, neglecting the higher order terms for small P . This can be rewritten to give $P/E \propto 1/(T - T_0)$.

Returning to equation (1-2) for the definition of the dielectric constant, we have

$$\epsilon = 1 + 4\pi (P/E) = 1 + \frac{4\pi /C}{(T - T_0)},$$

which is of the same form as the Curie-Weiss law, equation (1-7), that we developed from the Clausius-Mossotti relation using classical electrostatics which also predicts the occurrence of an infinite value in the dielectric constant at T equals T_0 .

Thus we have seen that if there is sufficient interaction between the local field and a dipole in a medium, there exists the

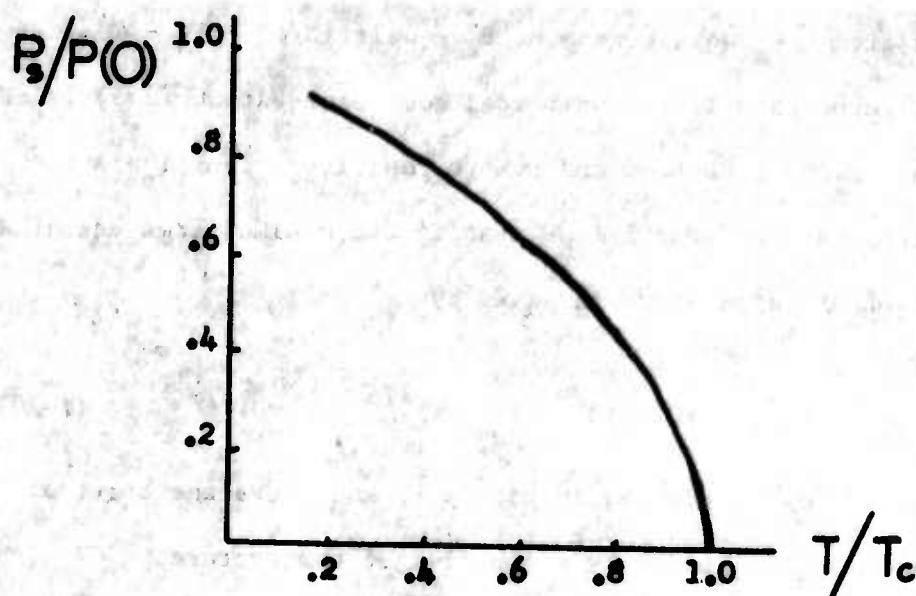


Figure 1

Spontaneous Polarisation versus Temperature

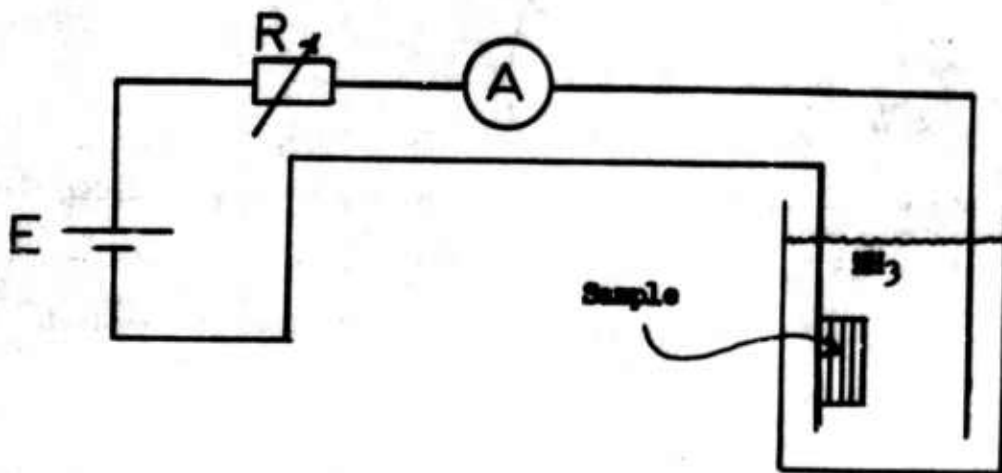


Figure 2

Electrolytic Reduction Schematic

possibility that at some critical or transition temperature spontaneous polarization occurs and the dielectric constant approaches infinity. However our considerations have neglected all other interatomic interactions, some of which may prevent the onset of ferroelectricity.

Our second aim was to describe the nature of the lamellar graphite compounds. Lamellar or pyrolytic graphite crystallizes in a layered structure. In each layer carbon atoms are tightly bound to three other atoms, which are much closer (1.415 Å) than in carbon-carbon single bonds. The layers are bound together by weak bonds which results in a greater separation (3.35 Å) between layers. Natural graphite occurs in a rhombohedral form in which every third layer is superimposable (4). The tight C-C bonding is attributed to sp^2 type hybrid bonding, while the loose interplanar bonding is attributed to Van der Waals forces (4). It is because of this disparity between the strengths of forces in different directions maintaining the graphite lattice that foreign substances are able to expand and occupy the interplanar spaces of the graphite crystal without disrupting the carbon layer planes which they separate.

Although many substances react spontaneously with graphite to form lamellar compounds, ammonia is one of a few reactants that require an auxiliary oxidizing or reducing agent to form the resulting lamellar compound. Even then it does not enter by itself, but it enters in conjunction with another ionic species. In this project the author used the ammonium ion as the ionic species to carry the ammonia molecule into the graphite to form the electrolytic

lamellar graphite-ammonia compound. The bonding between the graphite and the foreign substance in lamellar graphite compounds is believed to be of an ionic nature. Hall coefficient measurements have shown without doubt that the electron population of the conduction band is altered in all lamellar compounds. The stability of compounds is also favored by the electrostatic interaction of the ionic species present, with the stability being greater if charges of like sign are far separated and those of unlike sign are close together. Spatial separation of like charges on the reactant is enhanced by non-ionized reactant atoms or molecules which are present, as is the case with ammonia. The non-ionized species act as a sort of spacer between atoms of like charge. Since a spacer is more effective the greater its polarizability, the presence of ammonia as a spacer enables reactants that do not ordinarily form lamellar compounds to form an ammonia-reactant-graphite compound, which can be attributed to the high dielectric constant of ammonia.

Structure determinations have shown that carefully prepared lamellar compounds exist in several concentration stages which differ in the number of carbon layers alternating, in a periodic manner, between single layers of reactant. No lamellar compound has ever been found to contain multiple layers of the reactant between two adjacent carbon layers. Invasion of the lamellar graphite by the reactant can occur either by simultaneous attack at all layer planes, or by stepwise invasion of a limited number of layers such that a specific array of planes will be completely

filled with the reactant before another set begins, leading to a progressively more concentrated compound. There is some evidence of simultaneous attack at all layer planes in the formation of the spontaneous lamellar compounds, while the formation of the electrolytic compounds seems to follow the progressive attack at individual planes (4).

A more difficult and less understood problem is the orientation of the individual reactant molecules within each layer. The reactant does not retain a structure similar to its solid state structure, nor does it assume a random arrangement as in a liquid state. Instead, the molecules of the reactant are arranged on a lattice which tends to be closely related to the adjacent graphite lattice, as in Figure 3. In concentrated compounds, the neighboring reactant layers appear to be laterally displaced.

Our third aim in this section was to show that, because of structural similarities to KFCT, the graphite-ammonia compound could exhibit ferroelectric properties. As previously stated KFCT crystallizes in a repetitive layered structure, every third layer being a layer of the hydrated water molecules. The planes of water molecules are spaced at a separation of 8.4 angstroms, with two planes containing potassium ions and ferrocyanide octahedra at distances of 3.0 and 5.4 angstroms above each plane of water molecules. In the plane containing the water molecules there are 6.9 water molecules per hundred square angstroms, resulting in a dipole density of 0.82 water dipoles per hundred cubic angstroms. KFCT undergoes a spontaneous transition and exhibits ferroelectric

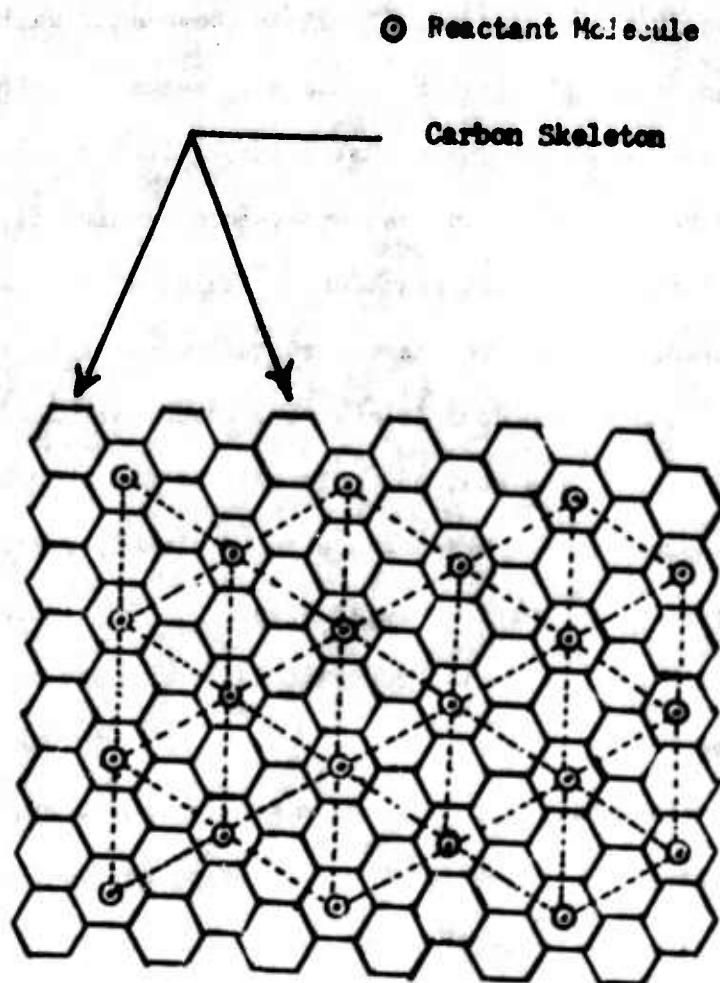


Figure 3
Carbon-Reactant Arrangement in $C_{6n}R_n$

phenomena below 247°K . The transition is of the order-disorder type where above the critical temperature the water molecule dipoles are in a state of rapid rotation and below the critical temperature are semilocked in place, spontaneous polarization being produced by the alignment of the water molecule dipoles. X-ray diffraction studies show that the heavy atom positions are unchanged on going through the transition temperature indicating that the spontaneous polarization may be accounted for by considering only the permanent water molecule dipole alignment (7).

If we assume Hennig's statement that graphite-ammonia compounds more concentrated than $\text{C}_{200}\cdot\text{NH}_4\cdot 4\text{NH}_3$ are unstable, that the lamellar graphite-ammonia compound has a reactant structure similar to that shown in Figure 3, and finally that a plane of ammonia molecules is located between each plane of carbon atoms, we have a resulting reactant concentration of 5.27 ammonia molecules per hundred square angstroms and a dipole density of 1.57 ammonia molecule dipoles per hundred cubic angstroms. Using this value for the dipole density and the commonly accepted dipole moment of 1.468 debye units for the ammonia molecule, we can compute a maximum value for the critical temperature of 97.1°K for the compound from equation (1-5). The same calculation for KFCT using 1.87 debye units for the water molecule dipole yields a value of 82.4°K which is not in good accordance with the experimentally determined value of 247°K . If we assume that the interaction of the dipoles to produce the local fields takes place within the planes of dipole

molecules only and there is no interaction between the planes, i.e., it is a two dimensional effect, we can calculate transition temperatures of 146 °K and 124 °K for the graphite-ammonia compound and KFCT respectively. The differences between the calculated value and the actual value of the transition temperature for KFCT can be attributed to discrepancies in our calculation of the local internal electric field, which indicates that the interaction between the permanent dipoles and the electric field, and the interatomic interaction between the dipoles themselves are much more complex than can be described by elementary theory.

However, since the structures of the lamellar graphite-ammonia compound and KFCT show so much resemblance to each other, coupled with the fact that similar transition temperatures can be calculated for each one, strengthen the postulate that the graphite-ammonia compound could exhibit ferroelectric phenomena.

2. Experimental Equipment

The experimental equipment necessary to form the lamellar graphite ammonia specimen consisted of a reaction vessel, Figure 4, a special sample holder, Figure 5, and an external electric battery used as an auxiliary reducing agent Figure 2.

The reaction vessel used for the electrolytic reduction of the graphite was a glass tube thermostated at 195 °K by immersion in an acetone-dry ice slush.

The sample holder incorporated the best features of several earlier models designed and built by the author. The sample holder was suspended from electrical terminals in an O-ring connector at the top of the reaction vessel. In view of the comment by Dzurus and Henning that platinum leads seem to catalyze the decomposition of the compounds, tungsten leads were used for all electrodes (3).

Since the expected resistance of the graphite specimen was to be in the vicinity of 0.2 ohms, an accurate measurement of its resistance could not be made with a Wheatstone bridge used in the ordinary way because of the relatively large uncertainty introduced by contact resistances at the binding posts. Therefore a Leeds and Northrup Kelvin Bridge, Model 4306, was used to measure the resistance. The fact that some of the measured resistances were much greater than expected will be discussed later.

The dielectric constant was determined on a resonance bridge, Figure 6, described by Sus et al for measuring the dielectric constant of materials with large conductivity (8). This bridge

From Temperature
Control Assembly

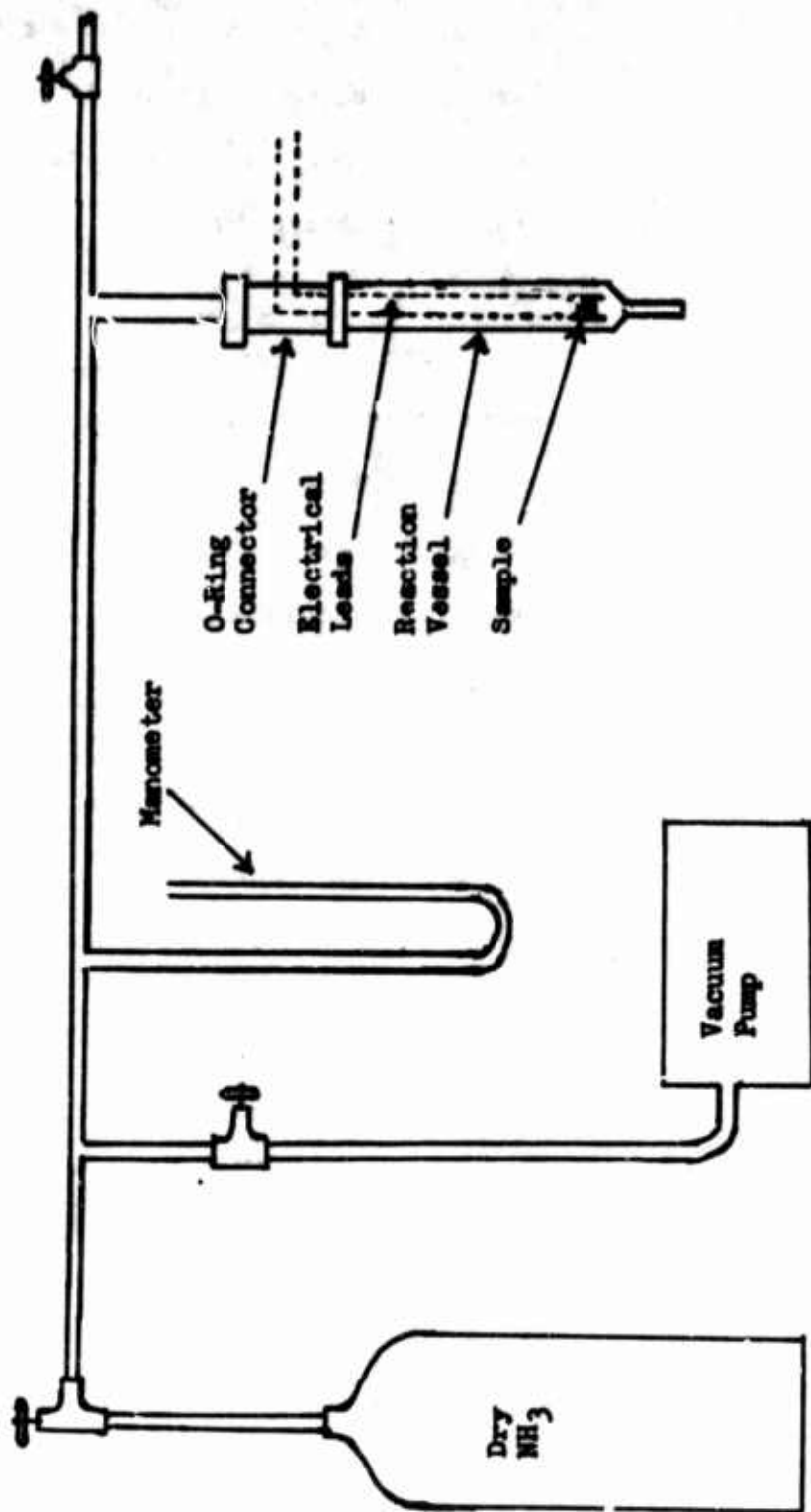


Figure 4
Reaction Vessel Assembly

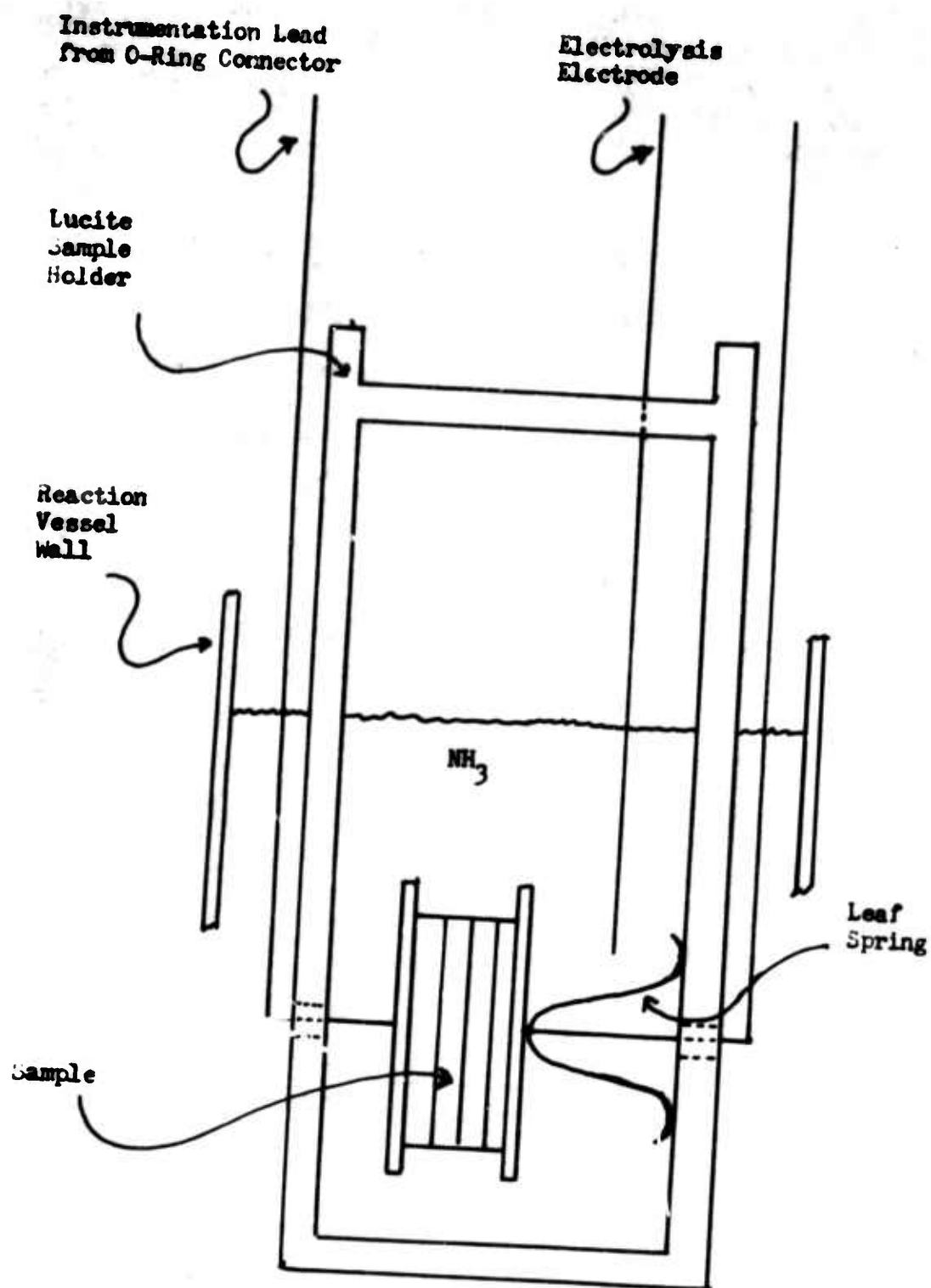


Figure 5
Sample Holder Assembly

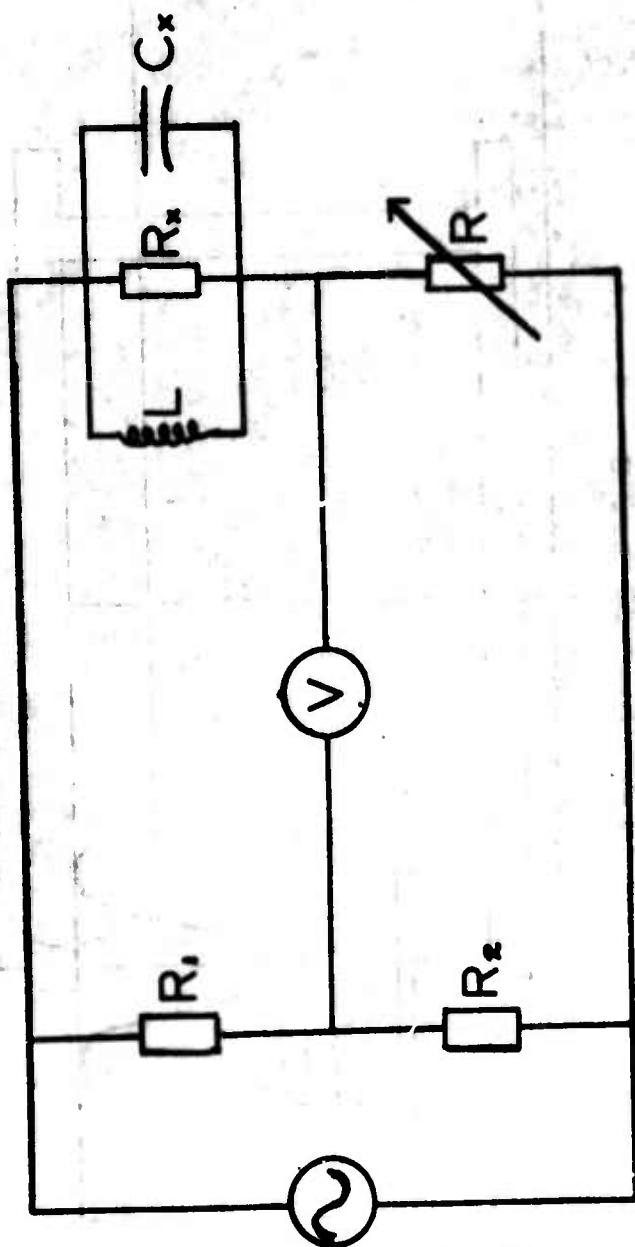


Figure 6
Resonance Bridge Schematic

utilizes the phenomenon of parallel resonance, and since the dielectric constant is determined by frequency measurements, its value can be measured with the greatest precision. In three branches of the bridge are placed active inductance free resistors R_1 , R_2 , and R . In the fourth branch was placed a parallel oscillating circuit, containing a known inductance L , and the unknown sample (C_x , R_x). Resistances R_1 and R_2 are identical. The balance of the bridge was determined on an oscilloscope. Adjustment of the bridge is accomplished by varying resistance R , and the input frequency ω . In contrast to other types of radiofrequency bridges, regulation of the resistance and the frequency can in practice be carried out independently of each other. At the resonant frequency $L-C_x$ presents a pure active resistance, and there are no reactive currents in the branches of the bridge. The dielectric constant, which is directly proportional to the capacitance, and the unknown resistance can be found directly from the obvious relations:

$$C = \frac{1}{\omega^2 L} \quad \text{and} \quad R_x = R.$$

A standard Navy AN/URM-25 RF Signal Generator set was used as an input to the resonance bridge. Signals from this set can be generated over a continuous range of frequencies from 10 to 50,000 khz. The RF output for the entire frequency range is continuously variable from 0.1 to 100,000 microvolts.

Temperature control for the dielectric constant versus temperature measurements was effected by a Varian, Model V-4257,

Variable Temperature System, Figure 7. The Variable Temperature System can provide automatic and precise control of the gas temperature around a specimen, and is commonly used in NMR spectroscopy. The parts which make up the system are: a copper tubing and glass heat exchanger, a 4 1/2 liter open top Dewar refrigerant container, and air transfer tube, and a temperature controller. The temperature controller is an electronic solid state instrument which contains the temperature controlling elements of the system. Temperature at the sample is controlled by passing controlled current through an electric heater in the gas stream directed to the sample. A resistance type temperature sensor, near the sample, monitors the gas stream temperature. The system is only capable of increasing the gas temperature in the gas stream. For temperatures lower than the normal ambient gas temperature the gas is passed through a heat exchanger coil submerged in a liquid nitrogen filled Dewar jar. The temperature control loop is closed around the controller, heater, gas stream, and sensor. The actual sample is down stream from the sensor and is not in the control loop. Therefore a chromel-alumel thermocouple was placed downstream from the specimen to measure the effluent gas stream temperature to obtain a more accurate sample temperature measurement.

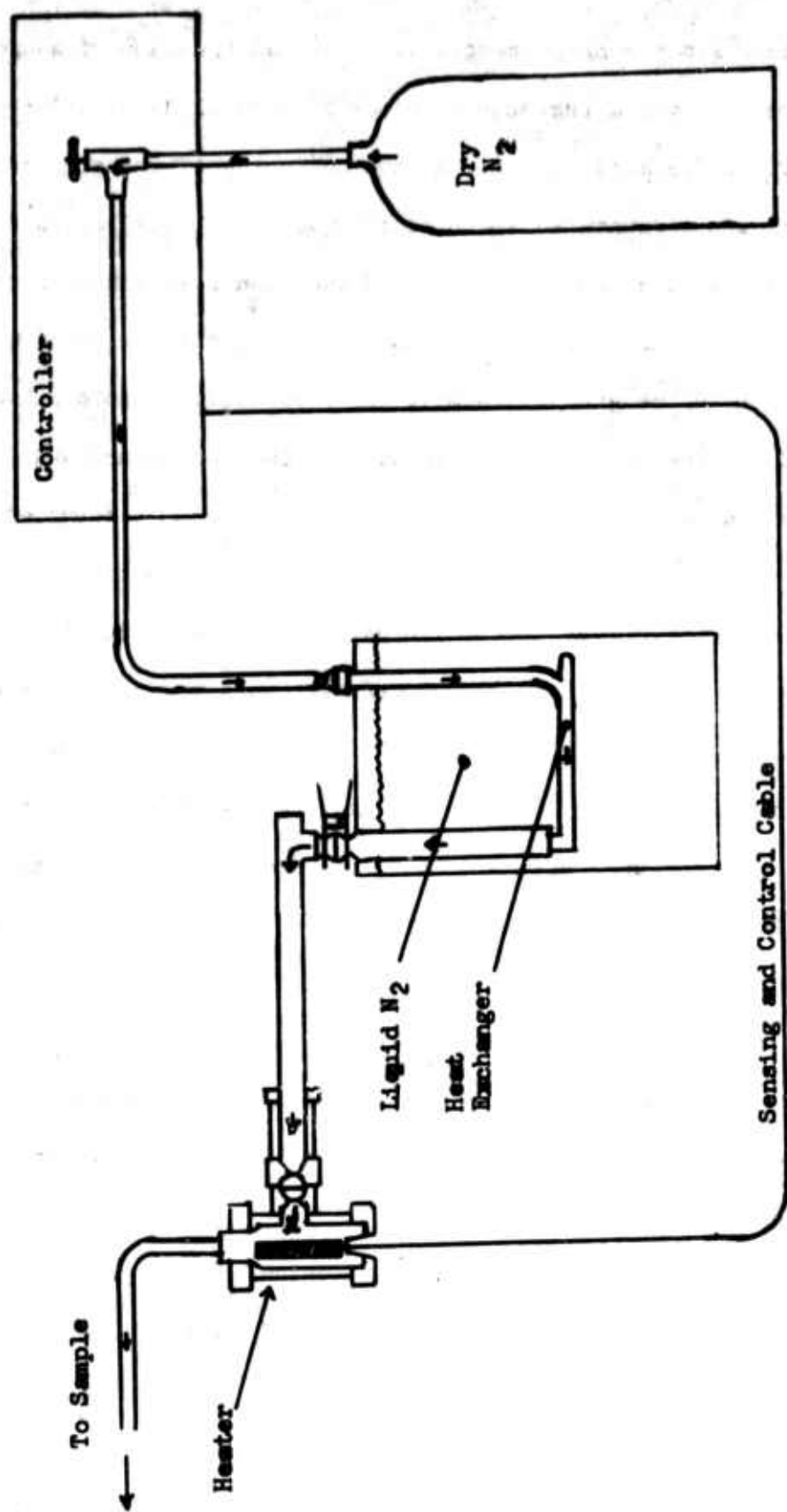


Figure 7
Temperature Control Assembly

3. Experimental Procedure

Each experiment commenced with the construction of a specimen. The specimen was a rectangular block of natural lamellar graphite 15 x 7.5 x 2.5 millimeters. At the beginning of the project difficulty was encountered in obtaining good electrical contact between the tungsten electrodes and the planar surfaces of the graphite. Mechanical pressure and silver conductive paint were tried. When the graphite sample was physically clamped between the electrodes, reasonable readings for the resistance and dielectric constant were obtained, but the mechanical pressure retarded the entry of the ammonia between the planes of the graphite to form the compound. The silver conductive paint on the surface of the graphite resulted in greatly improved electrical contact with much less mechanical pressure required on the part of the electrodes. The silver conductive paint, however, had the disadvantage that it would peel off the surface of the sample during the formation of the electrolytic graphite-ammonia compound. The most satisfactory method was to use a conductive epoxy resin on the surface of the graphite, and bond the graphite to two small stainless steel plates to which the tungsten electrodes had been silver soldered. The sample was then mounted in the sample holder and the assembly placed in the reaction vessel.

A small amount (0.1 gram) of ammonium nitrate was added and ammonia condensed into the reaction vessel until the sample was submerged. This resulted in a concentration of ammonium nitrate of 0.15 M in the liquid ammonia, the ammonium ion being the ionic species necessary to form the electrolytic lamellar graphite-ammonia compound.

Readings perpendicular to the planes of the graphite were now taken of the resistance of the sample, the resistance of the solution, and the frequency at which the resonance bridge balanced. After these preliminary steps had been completed, electrolysis was commenced. Total electrolysis times ranged from five to forty hours at an average current of 7.5 milliamperes. The electrolysis was completed in one hour intervals, with a set of readings being taken at the end of each hour.

When electrolysis was completed and the graphite-ammonia compound formed, the bottom tip of the reaction vessel was snipped off and the solution of ammonium nitrate in ammonia was allowed to run off into liquid nitrogen. At the same time the flow of dry gaseous nitrogen was commenced from the variable temperature system. The assembly was allowed to come to thermal equilibrium and then the frequency at which the resonance bridge balanced was determined as a function of temperature over the range 100 °K to 250 °K.

4. Discussion of Results

Eight samples were prepared for capacitance and resistance measurements. Capacitance versus temperature measurements were conducted on three of the samples. Figure 8 shows the results of the normalized resistance readings versus hours of electrolysis. The behavior of the resistance versus electrolysis curve does not show the orderly decrease in the resistance that has been observed by other experimenters. In fact an increase in resistance was noted in all samples where good electrical contact was made between the graphite and the tungsten electrodes. The author believes that this difference is due to the fact that in the previously published data spectroscopic or polycrystalline graphite was used, while this author used pyrolytic lamellar graphite. The increase rather than an expected decrease in the resistance can be attributed to the increase in the thickness of the sample as the graphite-ammonia compound was formed. The sample thickness increased by a factor of four during the course of the electrolysis and would have increased to a greater extent if it had not been physically confined by the sample holder. This increase in the sample size has not been reported in prior work on the graphite-ammonia compounds, although this may be the instability reported by Hennig for compounds more concentrated than $C_{200} \cdot HN_4 \cdot 4NH_3$ in polycrystalline graphite (4). It seems intuitive that the polycrystalline graphite wherein there are microcrystals of graphite in a random array so that there is no specific direction to the orientation of the graphite planes would show expansion to a lesser extent than the pyrolytic graphite where a layered structure exists throughout the

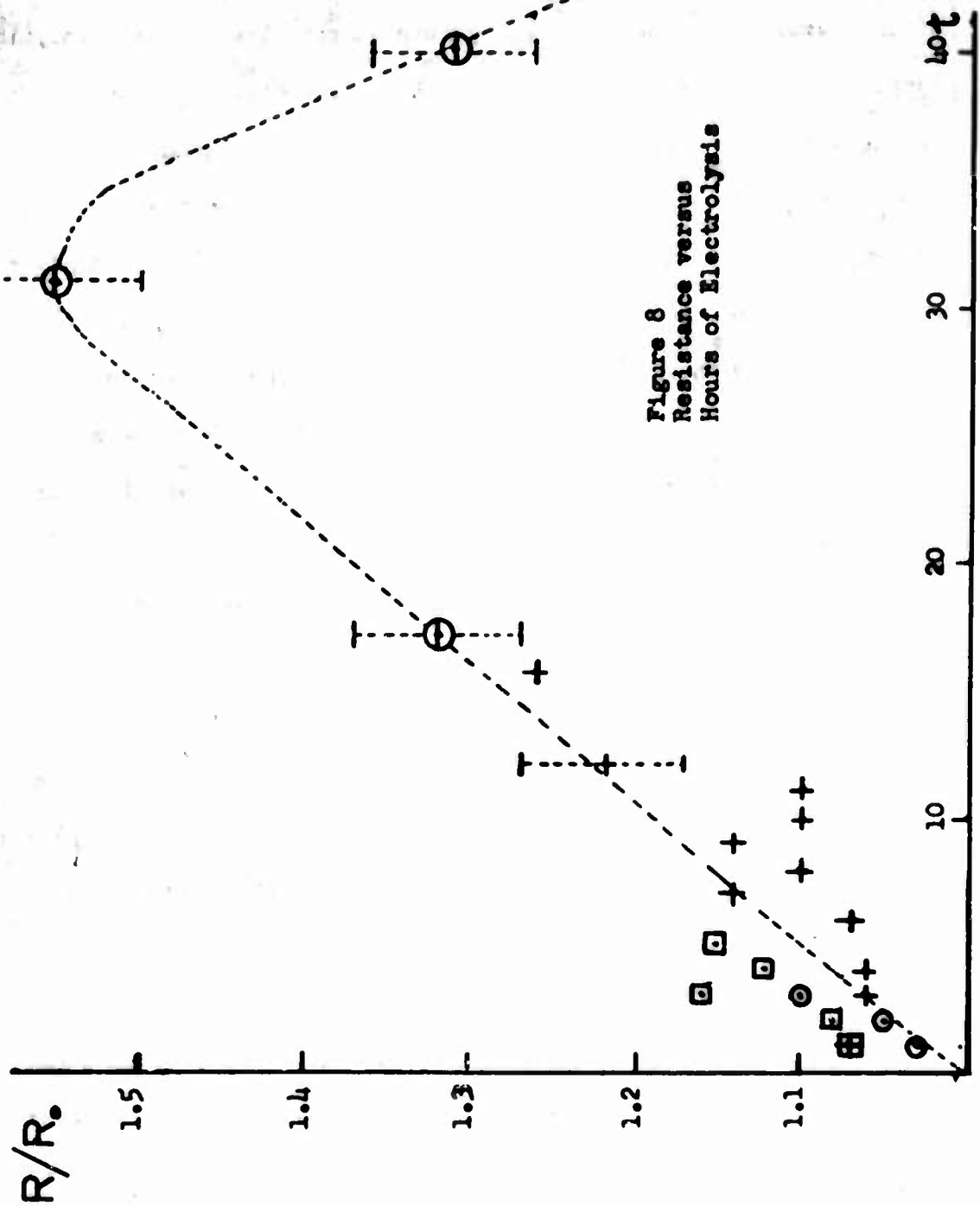


Figure 8
Resistance versus
Hours of Electrolysis

whole sample. In a private conversation Drurus implied that she and Jennig terminated their work on their samples when any deformation of the sample was observed. The growth in the size of the pyrolytic sample during electrolysis was small however compared to the increase in the thickness that occurred when the sample was warmed to room temperature. In all samples the odor of escaping ammonia was very evident as the sample warmed and increased in thickness in an almost explosive manner to a value fifty to sixty times its original thickness. Figure 9 shows a sample warmed to room temperature and a piece of graphite the original size. As can be seen in the photograph the warmed sample has a spongy appearance that is not at all like the original graphite.

The variation of the dielectric constant versus hours of electrolysis is shown in Figure 10. The results are in good agreement with calculated values for ϵ/ϵ_0 of 2.0 and 2.5 for graphite and the graphite-ammonia compound respectively. Although a continued increase in the dielectric constant was expected as the electrolysis was carried out, Figure 10 does show an initial increase with a subsequent decrease that can possibly be explained as an expansion effect analogous to that noted for the resistance.

In the resistance measurements specifically and to some extent in the dielectric constant measurements instabilities in the readings as a function of time only were noted. As the samples were allowed to sit variations in the measurements up to as great as twenty per cent were noted. These are the major contributing factor to the uncertainties in the data points shown in the curves.

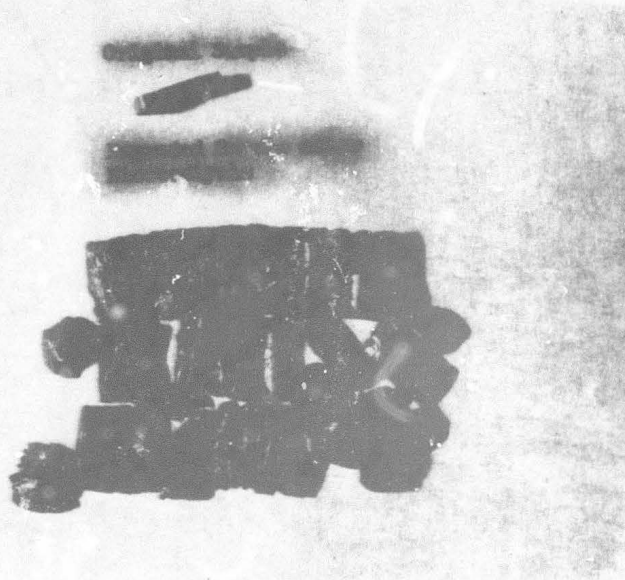


Figure 9

Expanded Sample after Electrolysis

Note: This phenomena of tremendous expansion was noted in all samples upon warming to room temperature.

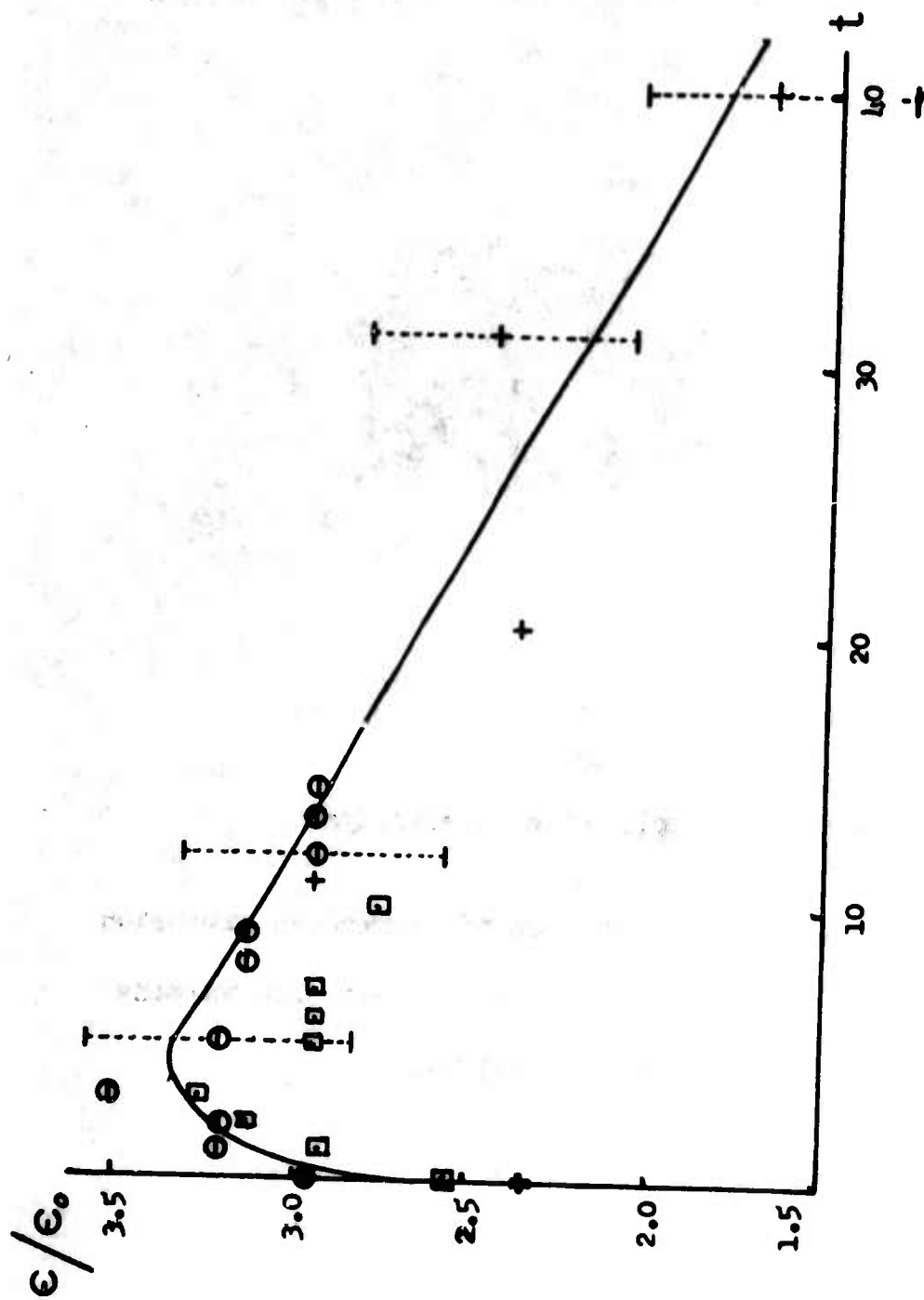


Figure 10
Dielectric Constant Versus Hours of Electrolysis

The dielectric constant versus temperature measurements shown in Figure 11 did not show the onset of ferroelectric phenomena, as would have been evidenced by a peak in the dielectric constant. In fact there appeared to be no temperature dependence at all. This could possibly indicate that the ammonia dipoles are hindered in their ability to rotate and align themselves with the electric field. One would expect that as the temperature, and hence the thermal agitation, decreased that the dipoles would become more aligned with the external field. This would result in an increase in the dielectric constant with a decrease in temperature (6). Although there was an indication that a ferroelectric state was possibly present in one of the sets of measurements as evidenced by a small peak in the dielectric constant the effect could not be reproduced.

Another source of difficulty encountered when using pyrolytic graphite as opposed to polycrystalline graphite was the fact that torque or lateral forces would cause the sample to cleave between two of the planes as the graphite-ammonia compound was being formed. Since cleavage of the sample destroys the experiment, this made the design and construction of the sample holder crucial.

A final fact that was noted as some of the samples were warmed to room temperature was that the entry of the ammonia between the graphite planes appeared to take place at all planes simultaneously as opposed to a stepwise invasion of a limited number of planes which Hennig states is the case for the electrolytic compounds. This was evidenced by the expansion that is shown in Figure 9 taking place only around the edges of the sample. This is probably

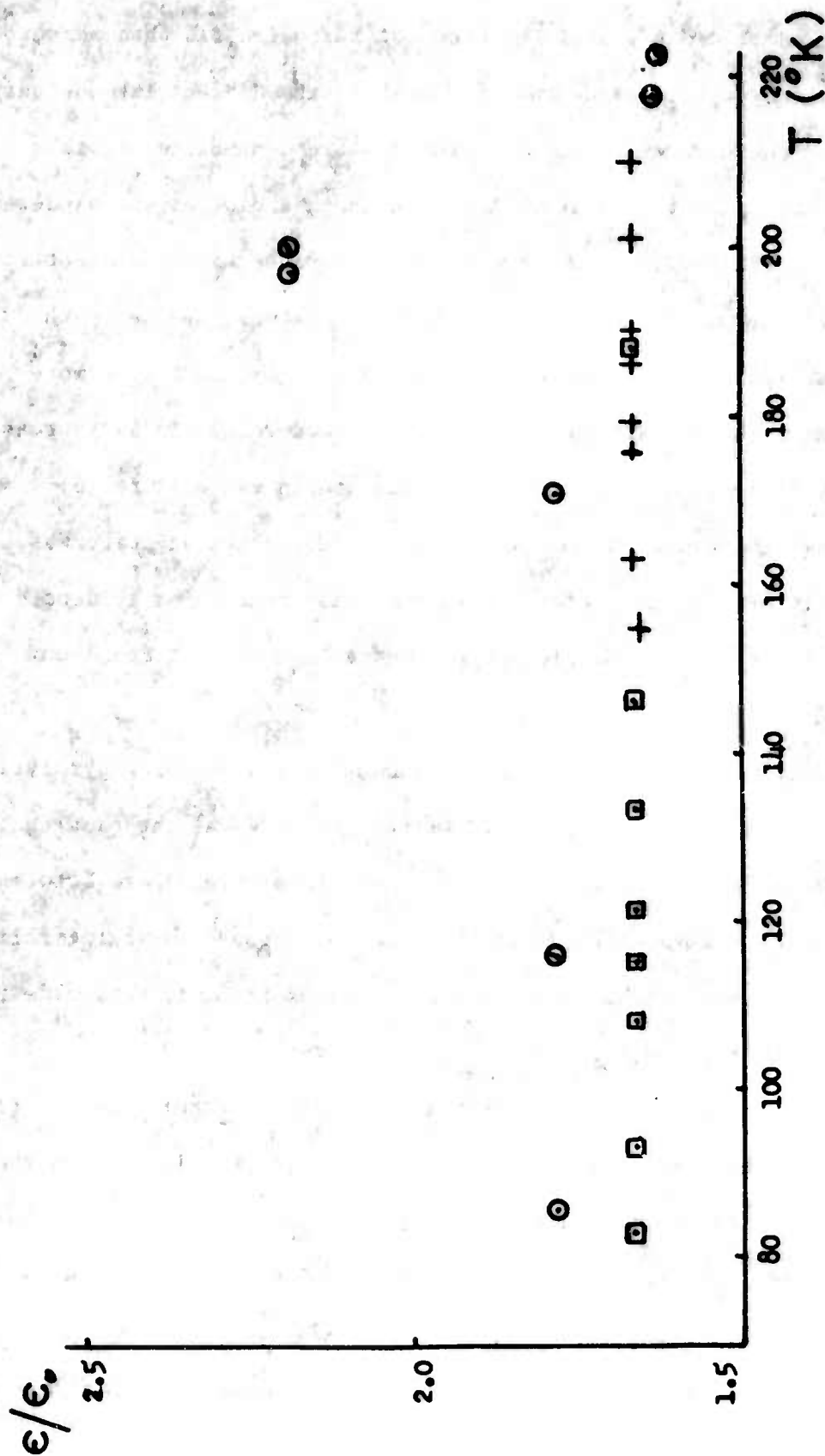


Figure 11
Dielectric Constant Versus Temperature

caused by the fact that the author used pyrolytic graphite rather than single crystal. Diffusion of ammonia into the graphite is undoubtedly impeded at crystalline interfaces.

5. Conclusions

The use of pyrolytic graphite for the formation of the graphite-ammonia compounds leads to results that are not consistent with those obtained using polycrystalline graphite. The author believes that these can be attributed to the differences in the macroscopic structure of the graphite, specifically to the great expansion of the graphite lattice that occurs as the compound is being formed in the pyrolytic graphite.

The fact that the onset of a ferroelectric condition was not observed was disturbing, but could possibly be attributed to an insufficient concentration of ammonia dipoles in the graphite lattice. This is correlated by the fact that the resistance measurements do not show the decrease that occurs in highly concentrated compounds. An indication of a ferroelectric state was observed in one of the sets of measurements, but it could not be reproduced. It is the feeling of the author that ferroelectric effects would be observed in highly concentrated compounds since the small peak that was observed was noted in the most concentrated compound that was prepared. A redesign of the sample holder that would permit the original sample to expand to ten to twenty times its original thickness and still maintain its rectangular shape would furnish a much more concentrated compound for use in investigating the ferroelectric effect.

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13. ABSTRACT

The theory of spontaneous polarization in ferroelectric solids leading to an infinite value in the dielectric constant is developed from classical electrodynamics and thermodynamics. The nature of the lamellar graphite compounds is discussed and similarities in the structure of one of these, the graphite-ammonia compound, to a recognized ferroelectric, Potassium Ferrocyanide Trihydrate, is pointed out. The details of the equipment and the procedures necessary to form the lamellar graphite-ammonia compound using pyrolytic graphite and to test the compound to determine if it exhibits ferroelectric properties are discussed. Ferroelectricity in the graphite-ammonia compound was not observed. Differences in the results obtained using pyrolytic graphite and those obtained using polycrystalline graphite by other observers to form the graphite-ammonia compound are pointed out and discussed.

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